



Carbon felt supported carbon nanotubes catalysts composite electrode for vanadium redox flow battery application

Guanjie Wei¹, Chuankun Jia¹, Jianguo Liu, Chuanwei Yan*

State Key Laboratory for Corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

HIGHLIGHTS

- A carbon felt (CF) supported carbon nanotubes (CNTs) catalysts composite electrode has been developed.
- The composite electrode improve the reversibility of the $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ redox couples greatly.
- The CNTs can be stabilized on the CF evenly and strongly by Nafion which is stable in vanadium solution.
- The VRFB single cell with the modified CF with MWCNTs content of 0.94 wt.% exhibits excellent performance.

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ABSTRACT

A modified electrode for vanadium redox flow battery (VRFB) has been developed in this paper. The electrode is based on a traditional carbon felt (CF) grafted with the short-carboxylic multi-walled carbon nanotubes (MWCNTs). The microstructure and electrochemical property of the modified electrode as well as the performance of the VRFB single cell with it have been characterized. The results show that the MWCNTs are evenly dispersed and adhere to the surface of carbon fibres in the CF. The electrochemical activities of the modified CF electrode have been improved dramatically and the reversibility of the $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ redox couples increased greatly. The VRFB single cell with the modified CF exhibits higher coulombic efficiency (93.9%) and energy efficiency (82.0%) than that with the pristine CF. The SEM analysis shows that the MWCNTs still cohere with carbon fibres after charge and discharge test, indicating the stability of the MWCNTs in flowing electrolyte. Therefore, the composite electrode presents considerable potential for the commercial application of CF in VRFB.

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1. Introduction

In recent years vanadium redox flow battery has received great attention as one of important energy storage technologies due to its various advantages, such as long cycle life, high efficiency, flexible design, high reliability, low maintenance costs and environmental friendliness [1–4]. As in other batteries, electrodes also play an important role in VRFB. The typical electrode materials for VRFB are metal and carbon materials. Metal materials such as noble metals and their oxides are not practical in VRFB because of their high cost and low specific area. Whereas, carbon materials, for example carbon felt, carbon paper and graphite powder, are widely used in VRFB, since they maintain remarkable advantages such as high specific surface area, wide operation potential range, stability and

reasonable cost [5,6]. However, the poor kinetics and reversibility of the carbon materials restrict their applications in VRFB. Although plenty of efforts have been devoted to modify the materials to enhance their electrochemical properties [7–11], the modified electrodes are not used in VRFB practically or not show excellent performance in the battery.

It is reported that the activity of the $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ redox couples on carbon electrodes are strongly influenced by the concentration and nature of the oxygen functional groups on the electrode surface [12–14]. Lu et al. reported that carbon fibres with high hydroxylation can provide more active sites for the vanadium redox reaction and make it more active [15]. Modifying CF with acidic oxygen functional groups such as hydroxyl, carbonyl and carboxyl groups seems to be a promising method to enhance their electrochemical activities. Due to the prominent physical and chemical properties, Carbon nanotubes (CNTs) are widely used in fuel cells as catalyst support [16–19]. It is also reported that the CNTs are used in VRFB as electrode catalysts ascribed to their high

* Corresponding author. Tel.: +86 24 2399 8320; fax: +86 24 2388 0201.

E-mail address: jck2003bx@yahoo.com.cn (C. Yan).

¹ These authors are contributed equally to this work.

surface area and super electrical conductivity [20,21]. Especially, Li [22] explored the different catalytic properties of three kinds of MWCNTs (Pristine MWCNTs, hydroxyl MWCNTs and carboxyl MWCNTs) toward $\text{VO}_2^+/\text{VO}^{2+}$ redox couples on a glassy carbon electrode by cyclic voltammetry and drew the conclusion that the catalytic property of the carboxyl MWCNTs is the best. However, because the carboxyl MWCNTs were loaded on the CF with no adhesion, and the loading of the carboxyl MWCNTs may not be stable enough to meet the challenge of washing out by flowing electrolyte in VRFB, the article only presented the performance of the modified CF as positive electrode in a static battery. The behavior of the modified CF in a flow battery had not been investigated.

In this regard, a new method is proposed to modify the CF electrode aiming at strengthening the stability of the carboxyl MWCNTs on the carbon fibres accompanied by obtaining excellent catalytic properties: the perfluorosulfonic acid polymer (Nafion) served as the agglomerant and attached the carboxyl MWCNTs onto the CF to form an integer composite electrode. In this way, the stability of the MWCNTs on the carbon fibres in flowing electrolyte is guaranteed by Nafion. The composite electrode was tested in VRFB practically and exhibited excellent electrochemical activity and durability. The method presented in this paper shows prospect to modify the CF electrode in VRFB for commercial application.

2. Experimental

2.1. Materials

The PAN-based CF (thickness: 4 mm) was produced by Shenhe Carbon Fibre Materials Co. Ltd. The MWCNTs (length: 0.5–2 μm , diameter: <8 nm, purity: >95%) were obtained from Nanjing XFNANO Materials Tech Co. Ltd and used as received. The 5 wt.% Nafion solution was got from DuPont and was diluted to 0.02 wt.% Nafion solution with ethanol.

2.2. Preparation of the composite electrode

The composite electrode was prepared as follows. Firstly, the pristine CF was washed in distilled water by ultrasonication for 30 min, and then dried at 100 °C for 2 h. Secondly, the carboxyl MWCNTs was added to 0.02 wt.% Nafion solution under agitation. Thirdly, the purified CF was immersed in the 0.02 wt.% Nafion solution after the carboxyl MWCNTs were well dispersed and suspended in the solution. Then the suspension with CF was treated by ultrasonication for 10 min. Finally, the modified CF was taken out of the suspension and was dried at 100 °C for 6 h. After the ethanol solvent vaporized, the carboxyl MWCNTs would be adhered onto the carbon fibres by Nafion.

The MWCNTs were mixed with the 0.02 wt.% Nafion solution as the ratios of 1 mg mL^{-1} , 2 mg mL^{-1} and 2.5 mg mL^{-1} to prepare the suspensions. In order to investigate the effect of the CFs size on its adsorption capacity, the CFs with different size were immersed in the suspension with the ratio of the MWCNTs to Nafion solution of 2.5 mg mL^{-1} . The related experiment parameters are listed in Table 1. In order to study the relationship between the loading of the MWCNTs on the CF and the quantity of them in the suspension, the CF with same size was immersed in the suspensions with three kinds of concentration mentioned above. The related experiment parameters are listed in Table 2. The content of the MWCNTs stabilized on the CF was calculated as the formula (because the quantity of Nafion cohering with the carbon fibres is quite small, the increase of CFs weight introduced by Nafion can be ignored):

Table 1

The parameters and research result for adsorption capacity of the CF with different size.

Parameters	1	2	3	4	5
Size of the CF/cm × cm	1.5 × 1.5	2.5 × 3.0	5.0 × 6.0	6.0 × 7.5	8.5 × 8.5
Volume of the CF/cm ³	0.9	3	12	18	28.9
Mass of the MWCNTs/mg	7.6	25	100	150	250
Volume of the Nafion solution/mL	3.0	10	40	60	100
Content of the MWCNTs/%	4.53	4.47	2.87	2.21	2.20

$$\text{Content} = \frac{W_{\text{after}} - W_{\text{before}}}{W_{\text{before}}} \times 100\%$$

where W_{before} is the weight of CF before modification; W_{after} is the weight of CF after modification.

2.3. Characterization of the composite electrode

The surface morphology and component of carbon fibres in the CF were analyzed by FEI INSPECT F scanning electron microscopy (SEM). The surface analysis was carried out by X-ray photoelectron spectroscopy (XPS).

2.4. Electrochemical tests

For cyclic voltammetry (CV) measurement, a three-electrode cell was used with the CF as the working electrode, a saturated calomel electrode as the reference electrode, and a Pt electrode as the counter electrode. The CF electrode was produced by sandwiching a piece of CF between two rubber sheets: the working area of one sheet was 1.286 cm², and on another sheet, a Pt thread was connected with the CF in order to collect the current. The analysis was performed in 0.1 M VOSO₄+2.0 M H₂SO₄ solution.

The charge and discharge test was carried out by using a VRFB single cell at a constant current density of 50 mA cm^{-2} . As for the cell, the conductive plastic plates were used as current collectors and a nafion 212 membrane (DuPont) served as a separator. The initial electrolytes for both positive electrode and negative electrode were 1.5 M VOSO₄+2 M H₂SO₄, and the volume of negative electrolyte was 80 mL while that of the positive one was 160 mL in order to avoid over-charging the positive electrolyte. The active area of each electrode was 28 cm². The upper and lower limit of the charge and discharge voltage was controlled to be 1.65 and 0.75 V, respectively. In order to reduce the experimental error, at least three different single cells with CFs (including pristine CF and modified CF) have been tested in the experiment and the related values were abstracted from these parallel tests' result.

3. Results and discussion

3.1. Adsorption rule of the MWCNTs

The modification of the CF is controlled by loading of the MWCNTs on it, and the loading of the MWCNTs is affected by the

Table 2

The parameters and research result for loading of the MWCNTs on the CF immersed in the suspensions with different ratio of the MWCNTs to Nafion solution.

Size of the CF/cm × cm	Content of the MWCNTs/%		
	Ratio of the MWCNTs to Nafion solution/mg mL^{-1}		
1	2	2.5	
2.5 × 3.0	1.50	3.27	4.47
8.5 × 8.5	0.94	1.68	2.20

adsorption capacity of the CF and the quantity of MWCNTs in the suspension. The physical properties of the CF, such as the size of the CF, the specific surface area of the CF, the pore size and the distribution of these pores in the CF, affects its adsorption capacity. Taking into account the commercial application of the CF with large scale in VRFB, adsorption capacity of the CF will depend strongly on its size. As illustrated in Fig. 1, the content of the MWCNTs decreases with the size of CF increasing. The related parameters and research result are listed in Table 1.

Fig. 2 presents the relationship between the loading of the MWCNTs on the CF and the quantity of them in the suspension. The related parameters and research result are listed in Table 2. For the CF with the same size, the content of the MWCNTs increases with the quantity of them in the suspension increasing. Whereas, the content of MWCNTs on the larger CF (the size of it is 8.5 cm × 8.5 cm) is less than that of the CF with small size (which is 2.5 cm × 3.0 cm) after immersed in the suspensions with the same ratio of the MWCNTs to Nafion solution.

3.2. XPS analysis

The XPS survey spectra of the carboxyl MWCNTs are illustrated in Fig. 3. A wide scan spectra was obtained to identify the surface elemental compositions. As presented in Fig. 3(a), the major surface elements are carbon and oxygen and the quantities of them are 96.5 at.% and 3.5 at.%, respectively. The peak position for carbon is approximately at the binding energy of 284.1 eV and that for oxygen is at around 532.0 eV. As shown in Fig. 3(b), the carbon in C1s spectra has several electronic states. The main peaks at 284.1 eV and 284.6 eV are assigned to the carbon in sp^2 C=C and sp^3 C–C groups, the total quantity of them are 98.23 at.%. The weak peak at 286.3 eV corresponds to the carbon in C–O groups, the quantity of it is 0.01 at.%. The peak at 289.4 eV presents the carbon in O–C=O groups, the quantity of it is 1.76 at.%. From mentioned above, it can be seen that the oxygen functional groups on the MWCNTs are mainly carboxyl groups.

3.3. SEM image and EDS analysis

As shown in Fig. 4, the surface of the carbon fibres in the pristine CF and the CF immersed in the 0.02 wt% Nafion solution without the MWCNTs are smooth, while the surface of carbon fibres with the mixture of carboxyl MWCNTs and Nafion are rough and the

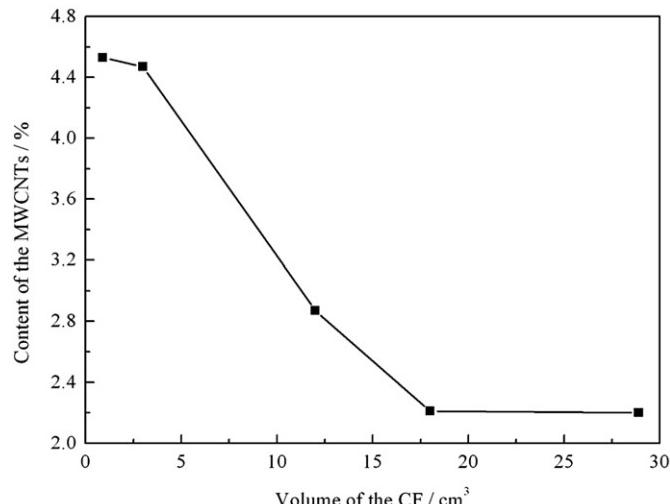


Fig. 1. Adsorption capacity of the CF with different size.

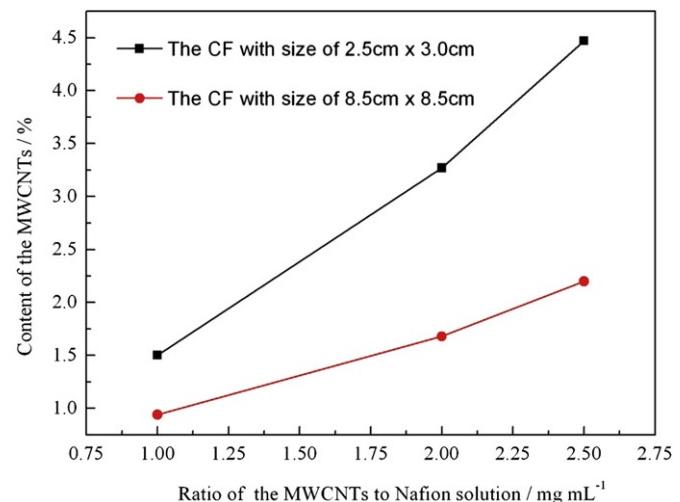


Fig. 2. Loading of the MWCNTs on the CF immersed in the suspensions with different ratio of the MWCNTs to Nafion solution.

roughness increases with the increase of the MWCNTs content loaded on the CF. Fig. 5 shows the morphology of the mixture on carbon fibres in the modified CF with MWCNTs content of 4.47 wt%. The image indicates that some of the MWCNTs on the carbon fibres are agglomerate presenting large particles, while some of them are

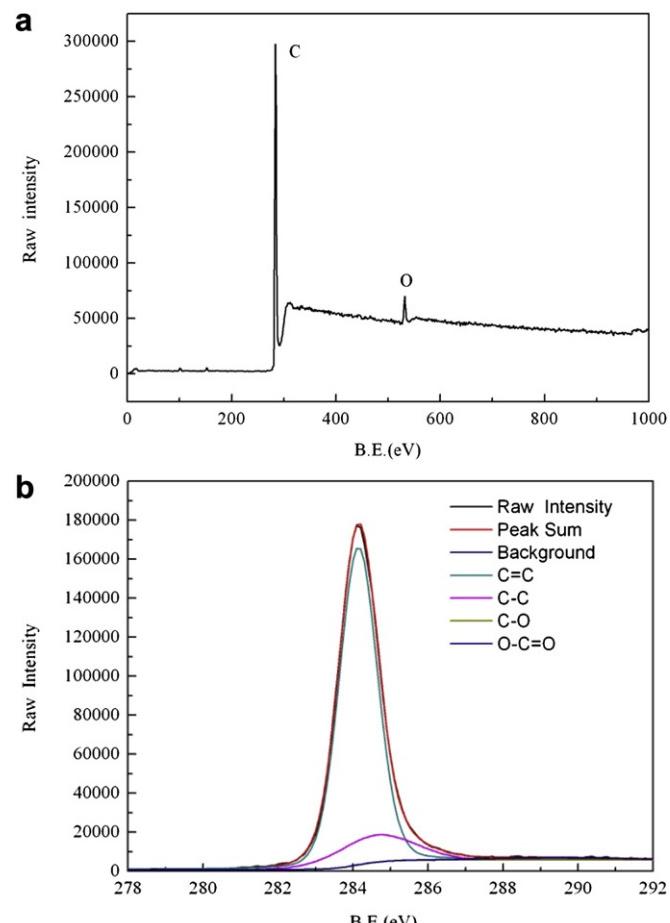


Fig. 3. General XPS survey spectra (a) and curve-fitting of the C1s from the carboxyl MWCNTs (b).

well dispersed with a ramiform structure. In order to investigate the component of the mixture loaded on the carbon fibres surface, EDS analysis is applied. The result shows that C, O, and F are found in the mixture and the content of each is 94.01 at.%, 4.31 at.%, 1.68 at.%, respectively. It indicates that Nafion also had loaded on the carbon fibres. Combining the result of EDS with the SEM images of MWCNTs, it can draw the conclusion that the MWCNTs are really stabilized on the surface of carbon fibres by Nafion. As shown in Fig. 6, the MWCNTs are well dispersed in different part of the modified CF leading to provide more active sites for the redox reaction during the charge and discharge test.

3.4. Cyclic voltammetry behavior

Fig. 7 presents the CV curves of $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ redox couples on CF electrodes (vs. SCE). The electrochemical parameters obtained from Fig. 7 are listed in Table 3. For the positive electrode, the oxidation peaks associated with the oxidation of VO^{2+} to VO_2^+

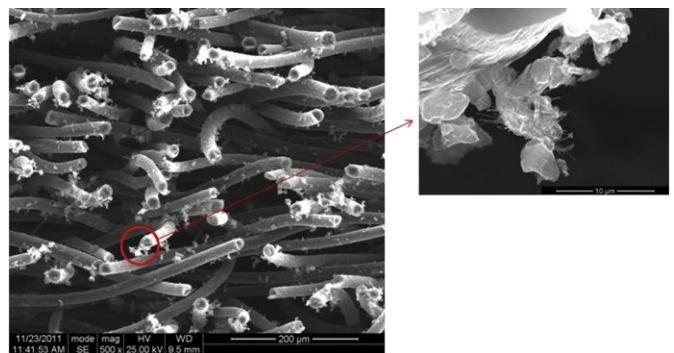


Fig. 5. Morphology of the mixture on carbon fibres in the modified CF with MWCNTs content of 4.47 wt.%.

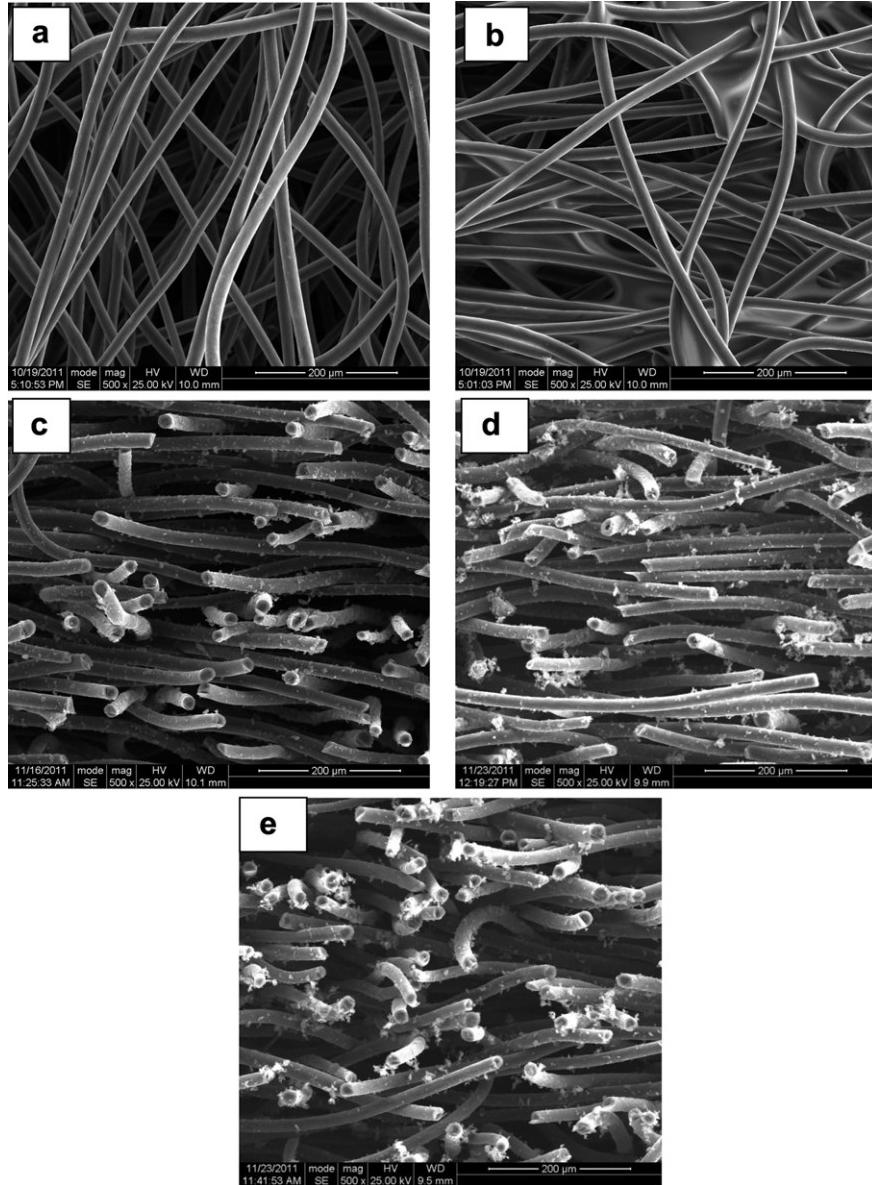


Fig. 4. Surface morphology of carbon fibres in the CFs: (a) the pristine CF, (b) the CF immersed in the 0.02 wt.% Nafion solution without the MWCNTs, (c) the modified CF with MWCNTs content of 1.50 wt.%, (d) the modified CF with MWCNTs content of 3.27 wt.%, (e) the modified CF with MWCNTs content of 4.47 wt.%.

and the corresponding reduction peaks appear at 0.9–1.1 V and 0.5–0.7 V (vs. SCE), respectively. For the negative electrode, the oxidation peaks associated with the oxidation of V^{2+} to V^{3+} and the corresponding reduction peaks appear at –0.3 to –0.5 V and –0.6 to –0.8 V (vs. SCE), respectively. The results demonstrate that CFs modified by the MWCNTs show much better electrochemical activity toward VO_2^+/VO^{2+} and V^{3+}/V^{2+} redox couples compared with the pristine one.

As shown in Table 3, the oxidation peak current (I_{pa}) and the reduction peak current (I_{pc}) of VO_2^+/VO^{2+} redox couples increase with the increase of the MWCNTs content. The reversibility of the redox couples also becomes better on the modified CFs. Among all the samples, the CF with MWCNTs content of 4.47 wt.% exhibits the best electrochemical activity for VO_2^+/VO^{2+} redox reaction, since it has small peak potential separations (ΔE_p) accompanied by a ratio of oxidation peak current and reduction peak current (I_{pa}/I_{pc}) closed to 1. Furthermore, the composite electrodes show much better electrical catalytic properties toward the reduction from VO_2^+ to VO^{2+} compared with that of oxidation from VO^{2+} to VO_2^+ . However, the CF immersed in the 0.02 wt% Nafion solution without the MWCNTs shows bad electrical catalytic property toward the redox reaction. This may be caused by the decrease of the active specific surface area which results from the coating of considerable Nafion on the surface of carbon fibres.

The improved activity of modified CF toward VO_2^+/VO^{2+} redox reaction mainly attributes to the catalytic properties of the carboxyl groups on the surface of the MWCNTs. The whole catalytic process of the reaction involves the following procedures: the transport of vanadium ions from the bulk of the solution to the surface of electrode and their ion-exchange with hydrogen ions in the carboxyl groups on the MWCNTs, the succeeding electron transfer or oxygen atom transfer, the ion-exchange with hydrogen ions again of the vanadium ions and their diffusion back into the bulk solution [12,13]. The catalytic mechanism of the electrode toward VO_2^+/VO^{2+} redox reaction is presumed as the group of formula from (1) to (3). Due to the carboxyl groups on the MWCNTs, the hydrophilic ability of the CF is improved and more active sites are introduced, as a result, more

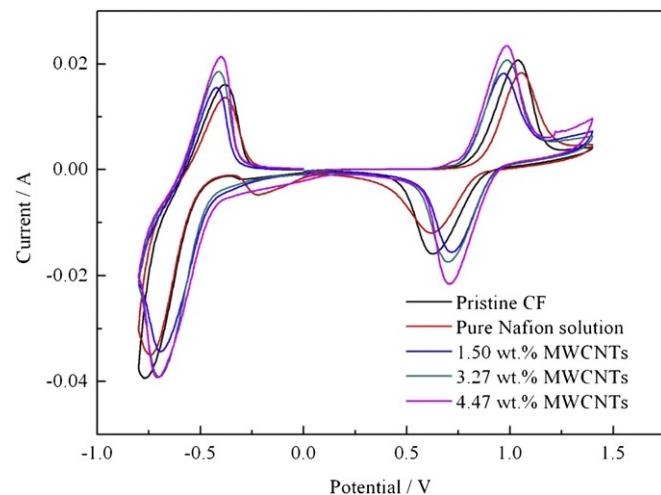


Fig. 7. CV curves of CFs recorded at 2 mV s^{-1} scan rates in $0.1 \text{ M VOSO}_4 + 2 \text{ M H}_2\text{SO}_4$.

reactive ions are adsorbed onto the electrode surface and attend the reaction. In addition, the electron transfer and oxygen transfer processes are also catalyzed by carboxyl groups, thus, these two processes become easier on the composite electrodes than on the pristine CF [14]. For the reason mentioned above, the reversibility of the VO_2^+/VO^{2+} redox couples on the modified CFs is greatly improved. The larger reaction current of the modified CF is ascribed to their more active sites for the redox reaction provided by the carboxyl groups [15]. On the other hand, it is also attributed to the improvement of the CFs electrical conductivity accompanied by the increase of the MWCNTs content [20].

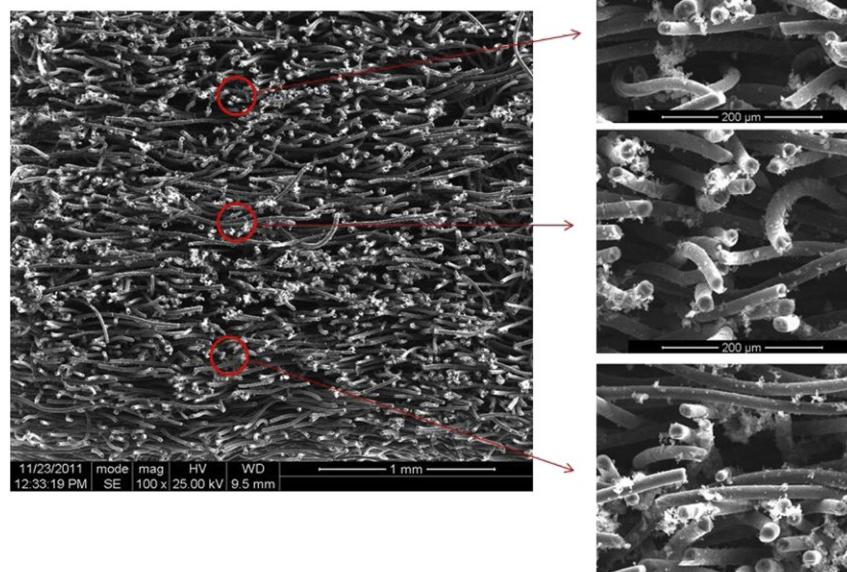


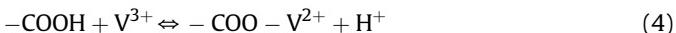
Fig. 6. General and local morphology of the modified CF with MWCNTs content of 4.47 wt.%.

Table 3

The parameters obtained from the CV curves for $\text{VO}_2^+/\text{VO}^{2+}$ on the CF electrodes.

Samples	I_{pa}/mA	$-I_{\text{pc}}/\text{mA}$	$-I_{\text{pa}}/I_{\text{pc}}$	$\Delta E_{\text{p}}/\text{V}$
Pristine CF	20.7	16.0	1.29	0.410
Pure Nafion solution	18.3	12.0	1.52	0.434
1.50 wt.% MWCNTs	18.2	15.6	1.17	0.252
3.27 wt.% MWCNTs	20.8	17.4	1.20	0.286
4.47 wt.% MWCNTs	23.4	21.6	1.08	0.278

The CV data of the composite electrode used as negative electrode are shown in Table 4. The electrochemical performance of the $\text{V}^{3+}/\text{V}^{2+}$ redox couples displays the same changing way as the content of the MWCNTs increases, while its reversibility is poorer compared with that of the $\text{VO}_2^+/\text{VO}^{2+}$ redox couples in general. Similar to the latter, the modified CF with MWCNTs content of 4.47 wt.% also exhibits the best electrochemical activity toward $\text{V}^{3+}/\text{V}^{2+}$ redox reaction. The catalytic mechanism on the improved activity of CF toward $\text{V}^{3+}/\text{V}^{2+}$ redox reaction by MWCNTs is similitude to that of the $\text{VO}_2^+/\text{VO}^{2+}$ redox couples. It is described as the group of formula from (4) to (6).



3.5. Performance of the VRFB single cell

The performance of the VRFB single cell with the modified CFs with different MWCNTs content has been tested, and the modified CFs served as both positive and negative electrode. The cell with the pristine CF has been also tested for comparing. The average efficiencies of the cell with different CF at a current density of 50 mA cm^{-2} are listed in Table 5. Compared with the cell using pristine CF as electrodes, the efficiencies of the cell with the modified CF are surely improved especially for the CF with MWCNTs content of 0.94 wt.%. According to the definition of the cell's reversibility, the improvement of the coulombic efficiency attributes to the advance of the cell's reversibility, and the cell's reversibility may mainly depend on the reversibility of the electrode. The increase of the voltage efficiency may owe to the catalytic properties of the carboxyl groups which introduce low polarization and decrease the overpotential during the charge and discharge process. As a result of the improvement of the voltage efficiency and coulombic efficiency mentioned above, the energy efficiency of the cell using modified CF with MWCNTs content of 0.94 wt.% as electrodes was about 82.0% (the energy efficiencies of three single cells with the modified CF were 82.0%, 83.1% and 83.2%, respectively). Despite of the fluctuations among the data, it also can be seen that the energy efficiency of the cell with the modified CF is at least 5% higher than that with pristine one (77.1%).

The data in Table 5 indicate that the voltage efficiency of the cell increases with the increase of MWCNTs content, while the coulombic efficiency deceases with the increase of it. As a result,

Table 5

VRFB single cell efficiencies for the pristine CF and the modified CFs.

Samples	Coulombic efficiency/%	Voltage efficiency/%	Energy efficiency/%
Pristine CF	90.5	85.2	77.1
0.94 wt.% MWCNTs	93.9	87.3	82.0
1.68 wt.% MWCNTs	92.2	88.6	81.7
2.20 wt.% MWCNTs	90.8	89.0	80.8

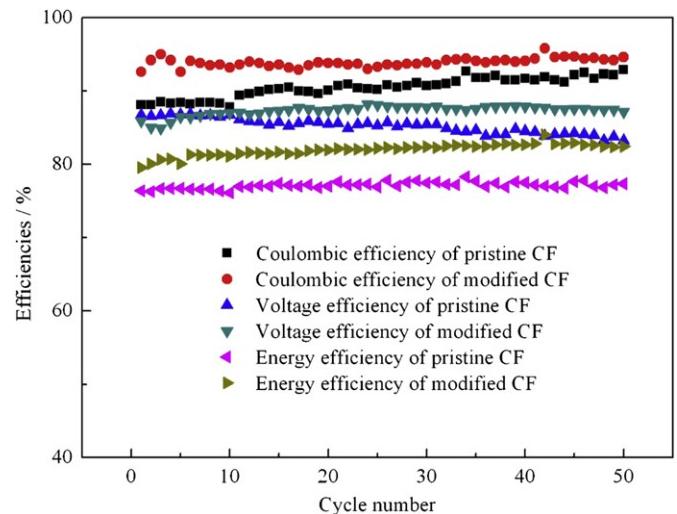


Fig. 8. Efficiencies of the VRFB single cell for the pristine CF and the modified CF with MWCNTs content of 0.94 wt.% at a current density of 50 mA cm^{-2} .

the energy efficiency decreases slightly. With the increase of MWCNTs content, more carboxyl groups are introduced onto the carbon fibres. Thus, the conductivity of hydrogen ions will be improved which is in favor of increasing the voltage efficiency. However, the diffusion of vanadium ions across the membrane will be stimulated leading to a decrease in the coulombic efficiency. Furthermore, with the increase of MWCNTs content, the overpotential of hydrogen evolution may decrease which will result in poor coulombic efficiency of the cell. The mechanism of the hydrogen evolution is under further investigation.

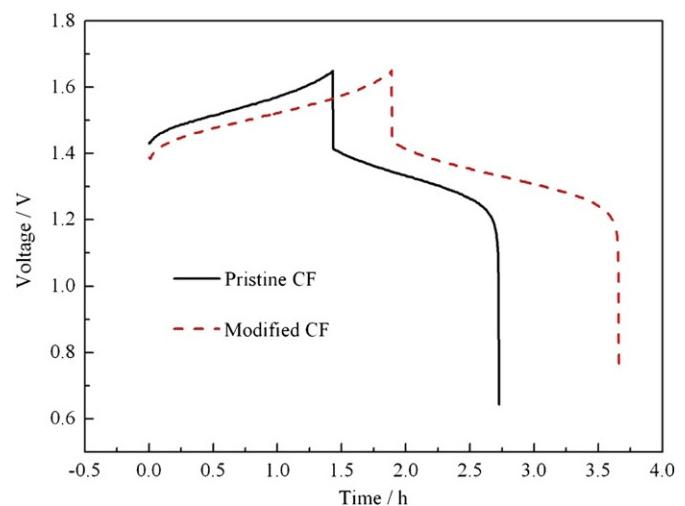


Fig. 9. The 15th charge and discharge curves of the single cell for the pristine CF and the modified CF with MWCNTs content of 0.94 wt.% at a current density of 50 mA cm^{-2} .

Table 4

The parameters obtained from the CV curves for $\text{V}^{3+}/\text{V}^{2+}$ on the CF electrodes.

Samples	I_{pa}/mA	$-I_{\text{pc}}/\text{mA}$	$-I_{\text{pa}}/I_{\text{pc}}$	$\Delta E_{\text{p}}/\text{V}$
Pristine CF	16.1	39.4	0.409	0.388
Pure Nafion solution	13.6	35.0	0.388	0.364
1.50 wt.% MWCNTs	15.5	34.4	0.450	0.272
3.27 wt.% MWCNTs	18.6	39.1	0.476	0.290
4.47 wt.% MWCNTs	21.3	39.3	0.542	0.308

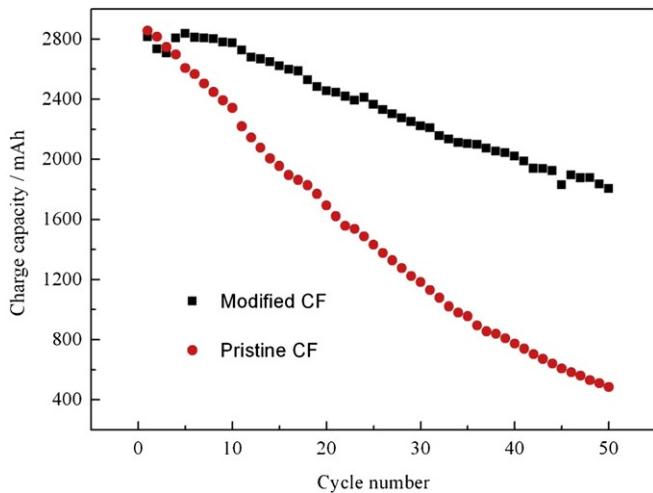


Fig. 10. The capacity decrease of the single cell for the pristine CF and the modified CF with MWCNTs content of 0.94 wt.% at a current density of 50 mA cm^{-2} .

Fig. 8 presents the efficiencies of the first 50 cycles for VRFB single cell using the pristine CF and the modified CF with MWCNTs content of 0.94 wt.% as electrodes at a current density of 50 mA cm^{-2} . As shown in the curves, the efficiencies of the cell with modified CF are higher than that of the cell with pristine one in general. In addition, the voltage efficiency of the cell with modified CF remains stable or even increases after several cycles while the cell with pristine one shows a decrease in voltage efficiency. The pristine CF should have been oxidized by vanadium solution and consequently the cell resistance with the pristine CF increases

leading to a larger overpotential. However, the carboxyl groups loaded on the modified CF suppress the oxidation of CF and the cell resistance presents no significant change.

Fig. 9 shows the charge and discharge curves of the 15th cycle of the cell with the pristine CF and the modified CF with MWCNTs content of 0.94 wt.% at a current density of 50 mA cm^{-2} , respectively. The curves show that the charge and discharge voltage of the cell with modified CF own smaller polarization than that of the cell with the pristine one, therefore, larger capacity is obtained. Fig. 10 shows the capacity decrease of the single cell with the pristine CF and the modified CF with MWCNTs content of 0.94 wt.% for the first 50 cycles. It can be seen clearly that the capacity decrease of the cell with modified CF is smaller than that with pristine one. As mentioned above, the voltage efficiency of the cell with modified CF remains stable indicating that the cell resistance of the modified CF is more stable than that of the pristine one during the charge and discharge test. Therefore, polarization for each cycle will remain the same for the cell with the modified CF, the capacity decrease of the cell caused by polarization will also be smaller than that of the cell with the pristine one. On the other hand, the perfluorosulfonic acid and carboxyl groups possess good hydrophilic ability which suppress the water transfer across the membrane and decrease the diffusion of vanadium ions. It is also in favor of obtaining smaller capacity decrease for the cell with the modified CF.

In order to investigate the stability of the MWCNTs on the CF, SEM is used to analyze the surface morphology of the carbon fibres in modified CF with MWCNTs content of 0.94 wt.% after charge and discharge test. As illustrated in Fig. 11, the surface morphology of the carbon fibres in modified CF after charge and discharge test shows no significant change compared with that before the test. The result indicates that the MWCNTs are stabilized on the surface of carbon fibres strongly in the modified CF.

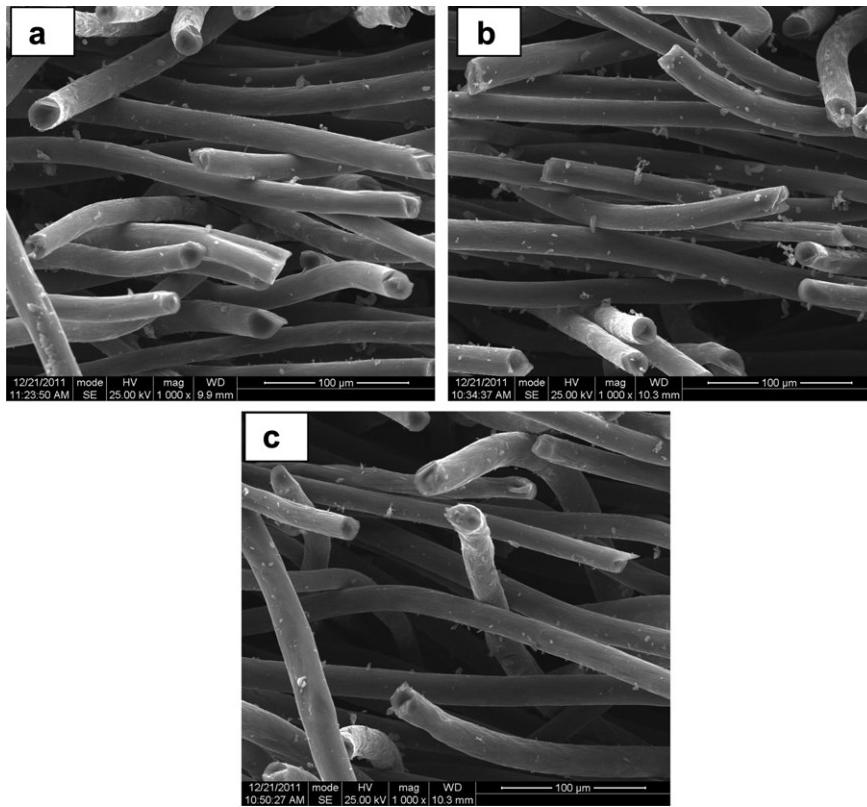


Fig. 11. SEM images of the CF with MWCNTs content of 0.94 wt.%: (a) the modified CF before charge and discharge test; (b) the modified CF acting as the positive electrode after charge and discharge test; (c) the modified CF acting as the negative electrode after charge and discharge test.

4. Conclusions

The MWCNTs have been stabilized on the surface of carbon fibres evenly and strongly in the CF. The electrochemical activity of the CF electrode has been improved with the increase of the MWCNTs content. The $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ redox couples show the best reversibility on the modified CF with MWCNTs content of 4.47 wt.%. Due to the improvement of the CFs' electrochemical properties, the VRFB using the CF with MWCNTs content of 0.94 wt.% as positive and negative electrode exhibits excellent performance. The advanced activities are mainly attributed to the catalytic properties of the carboxyl groups toward the redox reaction and the high electrical conductivity of the MWCNTs. In addition, the loading of the MWCNTs in flowing electrolyte maintains stable due to the adhesion of Nafion. With the inspiration of the results mentioned above, the method is considered an efficient way to modify the CF and the other catalysts also can be introduced onto the surface of carbon fibres in the same way. It is expected to make an improvement for the commercial application of CF electrode in VRFB.

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